Structure Model for Liquid Neopentane

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Synopsis. Structure simulation studies for liquid neopentane have been carried out by the use of real space expansion and reciprocal space expansion based on the local lattice structure model. A body centered cubic (bcc) model has reproduced Narten's experimental data very well.

X-Ray diffraction studies for liquid neopentane were carried out by Narten.[1] He measured the diffraction intensities from the liquid at eight different temperatures under high pressure from −17° (melting point) to 150 °C (cf. the critical point, 161 °C and 32 bar). He also attempted structure analysis, constructing an intermolecular correlation function from Percus-Yevick theory using the analytical solution for hard spheres. He reported that the calculated correlation function was in very good agreement with the experimental curves for values of $s \leq 1.5$ Å^{-1} but the deviation from the experimental intensity became large with increase of s ($s=4\pi\sin\theta/\lambda$).

In order to understand orientational correlation of molecular liquids, it is useful to construct a model in which we visualize a structure model which is to be tested against the experimental intensity. Such modeling for liquid structure, such as the "local lattice structure model" is usually formulated in the form of "real space expansion."[2-4] Recently a new method named "reciprocal space expansion" has been introduced by the present author and her coworker.[5,6] The real space expansion and reciprocal space expansion are complementary to each other; with good convergence in larger s-values for the former and the good convergence in the smaller s-region for the latter. The two methods were successfully applied to liquid carbon tetrachloride[4-6] based on the local lattice model of a bcc arrangement with head-tail head-tail packing.

In the present work the two methods have been applied to the structure simulation for liquid neopentane using the same bcc model. The diffraction intensities of liquid neopentane observed by Narten[1] are used.

First, the real space expansion was tried, and the weighted structure function $si(s)$ was used for the comparison of the simulated scattering intensities with the experimental ones. The least-squares refinement was carried out with four parameters; the lattice constant of the bcc cell a, the Prins parameter D,[7] the radius of the discrete structure region R_c and its temperature factor l_c. Because of the large values of l_{ij}, the more rigorous expression $\sin s(r_{ij}-l_{ij}^2/r_{ij})$[8] was used in the calculation instead of $\sin sr_{ij}$ of Eq. 4 in Ref. 4. For the values of the intramolecular distances r_{C-Me} and r_{Me-Me} and their root mean-square amplitudes l_{C-Me} and l_{Me-Me}, those obtained by the gas electron diffraction[9] were used. The group scattering factor for CH_3 group introduced by Narten[1] was used.

The number of molecules first contained in the discrete structure region was nine (a central molecule and the first nearest neighbors) at the initial trial, which was increased during the least-square refinements up to 51. That is the number of molecules included in the fourth nearest neighbors around the central molecule. Further increase of the number of molecules in the structure region no longer changed the feature of the calculated $si(s)$ curve. Scattering intensities ranging from 1 to 6 Å^{-1} have been used, because for the s-region smaller than 1 Å^{-1} spurious peaks inevitably appear whereas for the s-region larger than 6 Å^{-1} the calculated $si(s)$ is approximately equal to that of a free neopentane molecule and is considered hardly affected by the intermolecular interference. The results of the least-squares refinements for the

Table 1. The Refined Parameters of the bcc Model for Liquid Neopentane[a]

t/°C	a/Å	d/Å	D/Å	R_c/Å	l_c/Å	R factor[b]
−17	7.09(9)	6.14	0.057(16)	13.0(4)	1.8(8)	0.14
0	7.21(10)	6.24	0.058(16)	13.2(4)	1.9(10)	0.14
25	7.31(10)	6.33	0.069(17)	13.3(4)	2.1(10)	0.11
50	7.33(11)	6.38	0.074(18)	13.3(3)	2.2(9)	0.10
75	7.52(12)	6.51	0.091(25)	13.3(3)	2.5(9)	0.09
100	7.71(15)	6.68	0.113(35)	13.9(4)	2.1(10)	0.08
125	7.82(18)	6.77	0.128(48)	14.1(4)	2.3(12)	0.07
150	7.97(22)	6.90	0.151(51)	14.3(5)	2.6(16)	0.07

a) a: the lattice constant of the bcc lattice, d: the nearest neighbor distance calculated from a, D: the Prins parameter, R_c: the radius of the structure region, l_c: temperature factor for R_c. The values in parentheses are the standard deviations in the last significant digit. b) The reliability factor R is defined by

$$R = \left[\frac{\sum \{si(s)_{exp} - si(s)_{calc}\}^2}{\sum (si(s)_{exp})^2} \right]^{1/2}$$

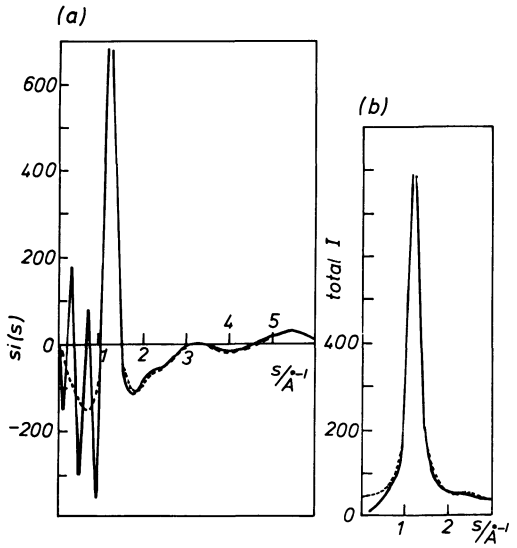

Fig. 1. The scattering intensities of liquid neopentane at −17 °C. The solid curves are the calculated intensities and the broken curves are Narten's experimental values. (a) Reduced intensity $si(s)$. The calculated one is obtained by the real space expansion based on the bcc model. (b) Total coherent intensity $I(s)$. The calculated one is obtained by the reciprocal space expansion.

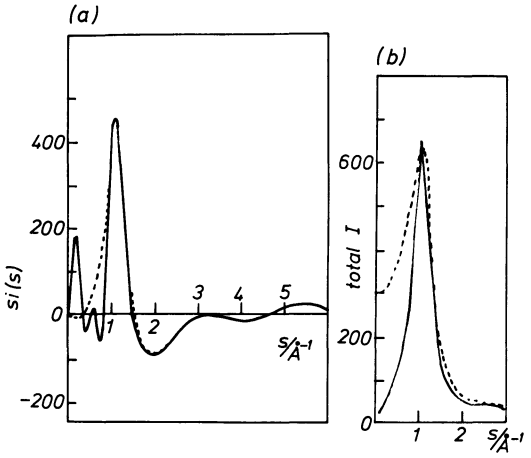

Fig. 2. The scattering intensities of liquid neopentane at 150 °C. See the caption of Fig. 1 for other details.

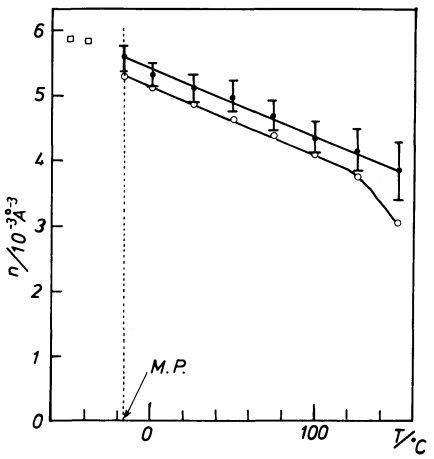

Fig. 3. Number densities n of neopentane. Dots show the values obtained by the bcc model, open circles those from Refs. 11 and 12 cited in Ref. 1 and squares for the plastic crystal phase.[13,14]

eight temperatures are shown in Table 1. The values of the nearest neighbor distance d are also given. The calculated $si(s)$ curves at −17° and 150 °C are respectively compared in Figs. 1(a) and 2(a) with Narten's experimental data.

Next, the reciprocal space expansion was carried out using the same a and D parameters. In this calculation reciprocal lattice points up to 600 are included. For the 600 the magnitude of the reciprocal lattice point vector is 5.32 Å^{-1} in the case of the data at −17 °C. The total coherent intensity is adopted, because it distinguishes the discrepancy between the experimental and simulated intensities in the small s-region. The results at −17° and 150 °C are shown in Figs. 1(b) and 2(b).

As seen in Figs. 1 and 2, X-ray scattering intensities from liquid neopentane could be well simulated by the bcc model, in the range of $s \geq 1$ Å^{-1} by the use of the real space expansion and in the range of $0.5 \leq s \leq 3$ Å^{-1} by the use of the reciprocal space expansion. Two peaks on the calculated curves at an s-region smaller than 1 Å^{-1} in Figs. 1(a) and 2(a) are all spurious due to the sudden onset of the continuum region to the discrete region, which do not appear in the total coherent intensity curves calculated by the reciprocal space expansion. A difference between the experimental and calculated intensities by the use of the reciprocal spece expansion is seen in the region of $s \leq 0.5$ Å^{-1}. The experimental scattering intensity near $s \approx 0$ Å^{-1} has a finite value because of the density fluctuation of the liquids.[10] With increase of temperature the density fluctuation increased and especially near the critical point this became significantly large. The density fluctuation was not included in the present formulation by the local lattice structure model.

From the variation of the lattice constants a's determined for the bcc model at different temperatures, the number densities of the liquid were calculated, these are shown in Fig. 3. The number densities decreased almost linearly with the increase of temperature. For comparison, the values tabulated in Narten's paper[1] are also given in Fig. 3. He obtained them by interpolating the values from the measurements of Gonzales and Lee[11] and from the values listed in the book by Timmermans.[12] The number density obtained from the present bcc model is approximately 5% larger than these values. The difference of these number densities may be explained by the possibility that the volatile neopentane contains many voids in its structure. The number densities for the plastic crystal at −40° and −50 °C calculated from values of the mass density determined by means of powder diffraction[13,14] are also shown in Fig. 3.

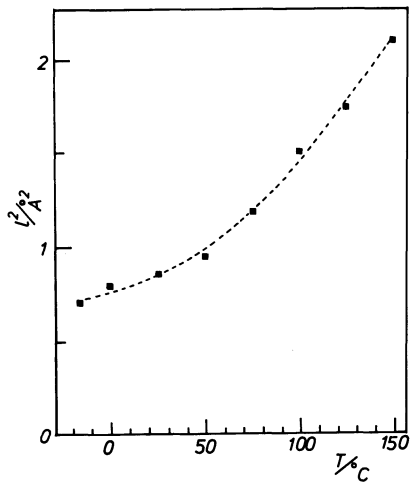

Fig. 4. Temperature dependence of the mean square deviation, l^2, of the neighboring neopentane molecules.

The mean square deviations of liquids increased as the distance between the central molecule and surrounding ones increased, and the deviations in the case of liquid neopentane were described well by the Prins relation $l_{ij}^2=2Dr_{ij}$.[7]

For harmonic oscillators at high temperature or low frequencies the mean square deviation of l^2 becomes[15]

$$l^2 = \frac{kT}{4\pi^2\mu\nu^2},$$

where ν is the frequency of the ocillator, T absolute temperature, and μ the reduced mass. Then l^2 is proportional to T. For several acceptable potentials with anharmonicity, the mean square deviation l^2 was calculated and found to be approximately proportional to T in this temperature range.[16] The observed l^2 was therefore expected to be nearly proportional to T. This however was not true in the present case, as is shown in Fig. 4. It exhibits a nearly parabolic increase with increase of temperature. This temperature dependence of the mean square deviations can be considered as the direct reflection of the effective potential that a molecule in the liquid feels. More detailed investigation on the mean square deviations will give information concerning the dynamical properties of the liquid but this is left for future studies.

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